PATENTS

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant(s): Huffman, et al. Examiner:

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For: NEW FORM OF CARBON

Assistant Commissioner of Patents
Washington, DC 20231

DECLARATION OF HAROLD W. KROTO UNDER 37 C.F.R. §1.132

Sir:

I, Harold W. Kroto, Ph.D., declare and say as follows:

1. I am the Royal Society Research Professor in the School of Chemistry and Molecular Sciences at the University of Sussex, Brighton, United Kingdom. For the convenience of the U.S. Patent Office, I have attached hereto as Exhibit 1 my curriculum vitae, which describes my credentials and demonstrates my expertise in the area of fullerenes.

2. I am intimately familiar with the literature concerning and was personally involved in the search for C_{60} and the greater fullerene family. For convenience, one may refer particularly to our review of the literature through 1990 described in an article entitled "C_{60} Buckminsterfullerene" in Chem. Rev. 1991. 1231-1235 attached hereto as Exhibit 2 and for my personal involvement in the research effort in my article entitled "C_{60}: Buckminsterfullerene, the Celestial Sphere that Fell to Earth" in Angewandte Chemie I.E.E. 1992, 31, 111-129 attached as Exhibit 3. I therefore believe it is fair to say that I am among the recognized experts in the subject of fullerenes.

3. I have reviewed the above-identified application. The application teaches in clear detail to the skilled artisan the preparation of fullerenes, including C_{60}, in quantities that were never recognizably achieved before the discovery by Huffman and Kratschmer described in the application. Specifically, the application describes the production of C_{60} and C_{70} in macroscopic amounts, i.e., amounts that could be seen with the naked eye. In addition, the application describes the preparation of substantially pure C_{60} and C_{70} and crystalline C_{60} and C_{70}. Their discovery for the first time permitted researchers to confirm the existence and structure of fullerenes including subjecting them to general testing of their detailed properties and characteristics, which had heretofore only been projected based upon educated speculation and calculation, grounded upon circumstantial evidence of their existence.

4. The realization by Huffman and Kratschmer of macroscopic quantities of fullerene and the isolation and characterization of C_{60} and C_{70} by the methods described in the above-identified application is recognized by the knowledgeable scientific community as a long awaited and much needed breakthrough; it was surprising that relatively high yields of fullerene such as C_{60} could be achieved by these methods, as it was expected that no more than < 1/10000 parts of fullerenes would exist in the soot product and that it would require very sophisticated equipment to isolate quantities of material required to establish and confirm the existence of the products. The difficulties that existed in the quest for C_{60} are well elaborated in the article entitled "Fullerenes" by Robert F. Curl and Richard E. Smalley, printed in Scientific American, Oct. 1991, pp. 54-62 attached hereto as Exhibit 4.

5. Although the discovery described in the Huffman and Kratschmer application may seem simplistic to the uninformed,

especially in hindsight, their discovery was quite remarkable. This is readily appreciated if one considers the historical perspective. Ever since the detection of C_{60} by the collaborative efforts of the Smalley and Kroto groups in 1985, as described in the article in Nature, 1985, 318, 162-163, attached hereto as Exhibit 3, experts, such as Drs. Smalley and myself, both together and separately worked to prepare fullerenes on a larger scale. For five long years, many attempts were tried, but each was unsuccessful. Finally, to my knowledge, one group, Huffman and Kratschmer, were the first to find a methodology capable of producing and isolating fullerenes, such as C_{60}, in macroscopic amounts. This methodology is described in their application and satisfied a long felt need in this area.

6. Furthermore, one should not underestimate the significance of their discovery. For the first time, scientists were able to produce and work with samples of fullerenes. They were able to confirm the theoretical prediction about fullerenes and continue to explore new properties of same. Their discovery spawned enormous scientific interest. As a consequence, innumerable investigations and studies relating to fullerenes were conducted, generating more than four thousand publications on the subject. In short, I cannot emphasize enough that their discovery revolutionized the area of fullerenes.

7. I have been ask to review the following two articles:

(a) "Fullerenes from the Geological Environment" by Peter Buseck, et al. in Science 1992, 257, 215-217 ("Buseck, et al.")

(b) "....and shower the Earth with buckyballs", by Jeff Hecht, New Scientist 1994 16 ("Hecht").

8. I have noted that both articles were published after Drs. Huffman and Kratschmer published their paper in Nature

1990, 347, 354-358, describing the specific production of macroscopic quantities of C_{60} and C_{70}, their isolation and characterization including the UV spectra of the C_{60}. A copy of this article is attached hereto as Exhibit 6.

9. Those facts in paragraph 8 are important since at the time of the publication of the articles cited in Paragraph 7 hereinabove, the skilled artisan in the field of fullerenes had samples of C_{60} and C_{70} in his possession. Unless special precautions are taken, it is very easy to contaminate samples having alleged trace amounts of C_{60} and C_{70} with these fullerenes. Contamination of the samples with fullerenes would obscure the results when working with low concentrations of C_{60} and C_{70}.

10. The Buseck, et al. article alleges that C_{60} and C_{70} were found in minute amounts in fissures in a rock identified as shungite, a carbonaceous rock found near the town of Shunga, in Karelia, Russia. It also alleges that the fullerenes are unevenly distributed in the fissures.

11. This article was and is still met with a certain amount of skepticism by the scientific community and the findings therein are highly controversial, even today. Many scientists tried to reproduce their results, but were unsuccessful. See, for example, "TECHNICAL COMMENTS" "Origins of Fullerenes in Rocks", published in Science 1995, 268, 1634-1635 attached hereto as Exhibit 7 wherein Ebbesen, et al. indicate that they were unable to obtain any fullerene from their sample of shungite.

12. I also am not completely convinced that the conclusions in the Buseck et al. article regarding the presence of fullerenes in shungite are correct. I also was able to obtain shungite rock from Russia, but was unable to find any evidence of the presence of C_{60} and C_{70} in these samples.

13. Another problem with the methods disclosed in the Buseck et al. article was the use of the laser technique to allegedly detect the C_{60} and C_{70} in their sample of shungite. As the skilled artisan is well aware, laser under certain conditions has been used to generate fullerenes. Even though reasonable efforts were made to allay suspicion in this regard, the paper does not entirely eliminate the possibility that C_{60} and C_{70} might have been produced during the sampling phase.

14. I also have queries about their findings for other reasons; I would have expected the whole range of related fullerenes to be found with any naturally produced C_{60} and C_{70}. Yet, Buseck, et al. did not report any such finding.

15. The Hecht article is a report by a third party, alleging that Dieter Heymann found C_{60} in New Zealand Clay. However, the article does not present any data or evidence of Heymann in support of the allegations therein.

16. The C_{60} and C_{70} described in these articles were allegedly found in trace amounts, in parts per billion. There are no large pockets of fullerenes, e.g., C_{60} and C_{70}, and where they are reported to be found, they are not reported to be found in macroscopic amounts. The amounts of C_{60} and C_{70} reportedly found are too small to be useful to the skilled artisan. It does not seem feasible that macroscopic amounts of C_{60} and C_{70} will be produced from mining these rocks.

17. Furthermore, when reportedly found in the natural environment, the C_{60} and C_{70} are never found as isolates. They are reported to be found as a part of a larger geological sample and are thus very impure.

18. Furthermore, the C_{60} and C_{70} reportedly found are alleged to be distributed in a matrix. It is my opinion that crystalline C_{60} and C_{70} have not been found in nature.

19. After reading these articles, I can say, without any reservation, that macroscopic amounts of C_{60} and C_{70} are not naturally found.

20. It is also important to note that there may be some confusion regarding the use of the term "soot". The soot referred to in the Huffman and Kratschmer application, which I shall call "fullerene black", is prepared by vaporization of graphite, in accordance with the procedure described therein. It contains the fullerenes, which are extracted therefrom. The "soot" in the Hecht article is believed to be derived from global forest fires at the end of the Cretaceous period. It is quite distinct from the "fullerene black." The "fullerene black" is also distinct from the soot produced during combustion of carbon in oxygen. The "fullerene black" in the Huffman and Kratschmer application is man-made and is not naturally produced.

21. I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true and further that any false statements and the like so made are punishable by fine or imprisonment or both under section 1001, Title 18 of United States Code and that such willful false statements may jeopardize the validity of any application or any patent issuing thereon.

Dated 27/7/95

Harold W. Kroto, Ph. D.